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For the Degree of Master of Science

Edgar Baruch

University of California

Berkeley, California

Dec. 6th, 1902

UNIVERSITY

ANALYSES OF A FEW WESTERN WOOLS

INCLUDING THE PARTIAL RESULTS OF A NEW METHOD FOR CLEANSING RAW WOOL

AND RESULTS OF INVESTIGATIONS ON THE ENSUING BY PRODUCTS.

Through the courtesy of Professor O'Neil opportunities were presented to work at these subjects in the chemical laboratories of the University of California. The work extended over a period of somewhat more than a year. The earlier part of the investigations were embodied in a partial report which was submitted in the contest for the "Faculty Prize" in Chemical Research in April, 1902.

The work in perfecting the apparatus for cleansing wool was continued without interruption until August, - after which time the investigations on the by-products was again resumed, - and is still in progress at the present time.

In June applications were made for patents on both the apparatus and the process for cleansing the wool. Most of the claims were lately rejected in lieu of those which had been filed by Edward Maertens of Providence, Rhode Island. (Vide U. S. Patents 698,207,-8,- 9,- 10,- 11, April 22, 1902.). There were however sufficient differences to warrant a contest, so the matter is still pending.

On June 16th of this year the Census Bureau published a bulletin by S. N. D. North on the "Utilization of Wastes and By Products in Manufacture". In it considerable attention is paid to the wastes of wool washing establishments. Mr. North points out many features of attempted improvement in modern methods of wool washing. There are many other similarities between his article and the one published by the author of this paper, several months previously. Any accus-

tion of plagiarism is, however, absolutely out of the question.

The author was totally unaware of Mr. Maertens' patents and those of others which deal with the subject of wool washing by the extraction method, by means of benzol etc., until after the rejection of the claims on the application for the patents filed.

Considerable original work was also done on the constitution of the wool-fat after which the author was very much discouraged to find that much of it had already been carried out by previous investigators. There was some satisfaction however in noting that the results of the work checked up very well with the previous investigations.

P A R T I.

ANALYSES, INVESTIGATIONS AND OBSERVATIONS OF SOME WESTERN WOOLS.

In 1897 through a mere cursory examination and analysis of a few samples of southern wools the author's attention was focused rather sharply on the composition of wools in general. It was not until August 1901 that the opportunity presented itself to again work at the subject, - though in the interim, the matter had frequently been thought of.-

The correlation between the analytical composition and the commercial value of raw wools seemed on first thought to be extremely important, and upon investigation really proved to be so. Before, however, noting the reasons for this correlation, allow me to impress upon the reader the importance of the wool industry. This can best be shown by a glance at the following figures.

In the year 1900-1901 there was produced in the United States about 305,000,000 pounds of raw wool, - South America produced about 510,000,000 pounds and Europe about 945,000,000 pounds. The world's production for the same year amounted to 2,685,000,000 pounds.

The United States plays no small part in the world's production, and of our supply the most of it, and the best at that, comes from

the Western States.

It is a notable fact that in the United States there is absolutely no scientific investigation of the qualities of the raw wools before they enter the market. Wools are bought and sold on the mere tentative examination of "experts". These men judge wools at a glance, in regard to elasticity and strength of fibre, with a precision of judgment that is astounding. But they claim to be able to estimate also the amount of moisture and dirt in the wools with the same nicety of judgment. It has been demonstrated repeatedly that it is impossible to judge the amount of moisture any closer than within a probable error of five per cent, while with dirt and dust the error ranges from one per cent to three per cent.

This being the case it is indeed ludicrous to note the bickering of merchants, who bargain to one-eighth and one-sixteenth of a cent when they are very apt to be making an error of judgment in their sales of from one-half to one cent per pound because of lack of proper scientific investigation. In Europe this possible source of error is duly considered by all intelligent merchants who submit samples of their wools to recognized "conditioning houses" where the samples are carefully and scientifically analyzed. There have been many improvements in late methods of investigation, and several inventions have very recently been made for the almost mechanical analysis of raw-wools.

It was a consideration of the lack of "method" in this country,

together with the curiosity to know whether or not one can attach any valuable connection between the grease content - and the strength and the elasticity of the wool-fibre, - which instigated the author's observations on western wools.

The samples of wool used were typical of the several portions of the country from which they were taken and cover fairly well all of the large Pacific States.

The first step taken in the investigations was the simple analysis of the raw-wool into its four main constituents (1) pure wool-fibre, (2) grease, (3) dirt, (4) moisture, and (5) supplementary to (1) the ash content of the pure wool. - The method of analysis pursued was as follows:

Ten grams of the raw-wool was sampled as carefully as possible.

The sample was then heated at 110° C for three hours and the moisture determined by difference.#

After drying, the grease was extracted from the wool by six hours' treatment in a Soxhlet Extractor, with water free ether. (After the treatment tests were made with osmic acid to be sure that all the fat

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The possibility of loss in weight by the loss of volatile constituents of the grease, was carefully considered. It would, had it occurred, have increased the percentage of moisture. Investigations showed however that it contained no volatile constituents under 130° C.

had been extracted). The wool was then dried and weighed and the fat was determined by difference, but the result was checked by weighing the fat in the receiver.

After the fat has been extracted the wool is easily freed from the dirt by mere immersion in hot water. The wool is then again dried at 110° C for one hour and the dirt is determined by difference. #

Below are tabulated all the averages ## ## of the analyses of the separate samples.

Wools.	Water	Grease	Dirt	Pure-Fibre	Ash.
Washington	9.35	35.8	28.15	26.70	1.40
Oregon	8.95	21.6	32.55	36.90	1.33
Nevada	8.70	21.2	38.05	32.05	2.90
Lake View (Nor. Calif.)	8.30	20.4	36.70	34.60	1.90
Bakersfield (So. Calif.)	5.75	23.8	42.65	77.80	2.80

This method of complete difference allows of opportunity for considerable error. Since, however, the chance error of sampling, far exceeds the possible error of analysis, - the errors brought about by the method of difference are practically, quite negligble. A complete check on the results can be established by washing the wool free from dirt in distilled water, then evaporating to dryness and weighing the residue (dirt).

There were from four to six separate analyses made of each sample.

Careful observation and interpretation of the above data shows numerous interesting facts, some of which might warrant general application. I have no doubt that the expert buyer and the wool grower would be able to give the same information - but from a different source, - that of experience only. The inference to be drawn from the data can be classed under the following heads:

I. - INFLUENCES AFFECTING MOISTURE. -

It is to be noted, as would primarily be supposed, that the percentage of moisture varies not so much with the quality of the wool fibre itself as with the quantity and quality of both the dirt and the grease. If the dirt in the wool is silicious or calcareous in character the amount of water which it is capable of retaining is necessarily small, if on the other hand the dirt is earthy or adobe-like as that which is mixed with wool from the southern ranges the amount of water is much increased. The amount of moisture that the grease can absorb varies as well as the dirt with the locality where the wool is grown. Grease from wool from mountain raised sheep contains more moisture than wool from the sheep of the southern ranges. It is obvious, though, that it is not so much the quality as the quantity of the grease which affects the percentage of moisture. The fibre itself is somewhat hygroscopic, but what things control this feature of the fibre, it would be hard to say. In general, these wools which have less ash have less moisture, the reason for which is that the

ash consists largely of potassium carbonate, a highly hygroscopic salt.

II. - INFLUENCES AFFECTING THE AMOUNT OF GREASE. -

The grease acts not only as a protective covering to the fibre but also as an additional means of retaining heat in the body of the animal, so it is naturally more abundant in northern than southern wools. Long fibred wool contains as a rule less fat than short fibred wool. Spring and summer wools have far larger percentages of fat than do autumn and winter wools.

III. - THE QUALITY AND QUANTITY OF DIRT. -

Both the quality and quantity of dirt, are features of the ranges on which the sheep are raised. Even short fibred wool raised on sandy soil contains more dirt than long fibred wool raised on firmer ground. Of course the primary factor influencing the quantity of the dirt is the soil, but a factor no less important is the grease, which if abundant matts all kinds of sod, dust, sand and effluvia in with the fibre. The quality of the dirt is an important point to which the attention will be drawn in another section of the paper.

IV. - THE ASH IN THE WOOL FIBRE. -

It was found that results showing the ash content of the fibre are valuable indices of the strength and elasticity of the wool. Fibre which contains a large percentage of ash is correspondingly low in Keratin. (Keratin is the essential constituent of the pure fibre. It

is, according to Hammersten, almost identical with the horny substance in hoofs, cartilage, horns etc.) It is the keratin which is elastic and lends strength to the fibre. The presence of mineral salts tends to make the keratin brittle and fragile. (Pure keratin being a complex organic compound should of course burn completely without leaving any ash).

Before closing this section of the paper it might be well to make further note of the hygroscopic nature of raw-wool by calling attention to the following extract from the Bulletin of the National Association of Wool Manufacturers. (Vol. 31).

"The amount of moisture which may be present in the fibre at any one time is largely dependent on the physical condition of the fibre together with the temperature and humidity of the atmosphere. Wool is capable of absorbing considerable and varying amounts of moisture without in the least altering its external appearance. In a warm dry atmosphere the average range of moisture in crude wools (western) is from 5-8%. The same wools range on cool damp days from 8-16%.

In addition to these variations the amount of moisture absorbed is also influenced by the nature of the grease and potash salts present in the fibre. It is a well known fact that western wools, in transportation to the eastern sea-board sometimes gain enough moisture in weight to

pay for their transportation East".

In France a standard of 18-1/4% moisture has been established for raw-wools. In this country absolutely no standards have as yet been established.

PART II.

INCLUDING THE RESULTS OF A NEW METHOD FOR CLEANSING RAW-WOOL.

(The subject in this section being such a broad one, it was found necessary to treat it in the briefest possible manner. Frequent references are made to processes in vogue, but detailed explanations of them are not given for they can be found in almost any work on technical chemistry. The works of Brant (Animal and Vegetable Fats and Oils, Vol. II), Blount & Bloxam (Chemistry for Engineers and Manufacturers, Vol. II) and Sadtler (Industrial Organic Chemistry) were referred to frequently for general facts. A complete bibliography will be found at the end of the section.)

In the spring of 1899, fully two years before the analytical work mentioned in Part I, the author had occasion to inspect a wool washing plant in Los Angeles, while visiting a number of other technical and chemical industries in that vicinity.

A number of interesting facts and some valuable data presented itself concerning the wool-washing industry. The plant established in Los Angeles had spent as an original investment the sum of $80,000. for property, building and machinery. At the outset of their career their apparatus and machinery proved unsatisfactory;

nearly the whole of it was removed and a complete new battery of washers was installed. The factory then ran for a while longer, rather unsuccessfully, under poor management. Finally, a short while after competent men were secured for the establishment, the plant suffered a sudden paralysis because of the sudden lack of local supply of raw wools, occasioned by the drought of 1899 - 1900. The production of the rest of the country was not diminished, but on the other hand increased, and the world's supply was overly large for the following two years; in consequence prices fell and remained at such a point that with the method of washing in use in that plant it became impossible to do further work. In the meantime the capital lay idle. During the latter part of the period of inaction the whole scheme was abandoned in disgust. The details have been mentioned in this case, because they are practically parallel with those of similar establishments all over the country.

The general failure of such local plants instigated some little thought. What were the advantages and drawbacks of such local institutions? These points were soon determined upon and shall be mentioned briefly.

The first point of obvious advantage which thrusts itself into view is the doing away with the deterioration of raw-wools in long storage and shipment. In substantiation of this fact it might be well to again quote from the Bulletins of the National Association of Wool Manufacturers:

"Growers have often been reminded that greasy wool does not improve in appearance and value by keeping; but probably not owners alone but even experts in the trade never had this truth so clearly revealed to them as during the season of 1899. A number of parcels after having been retained in local warehouses for twelve months, lost color to such an extent, and became so stained and sodden looking as to be quite unrecognizable. Buyers could not be prevailed upon to offer more than from 4-1/2c. to 5-1/2c. per pound for the wool, when at the beginning of the season they had offered from 12-1/2 to 13-1/2 c. for the same material.— A properly scoured wool can be held indefinitely without deteriorating, but if badly scoured the result is very similar to that experienced in the case of greasy wool. In other words it becomes as sodden as lead, discolored and extremely unattractive in appearance. Hence it is quite clear that if it is intended to hold the wool, the best course to pursue is to have it well scoured at the earliest possible period". This of course can be most easily accomplished by the establishment of local washing plants.

By following such a course the outrageous prices of transportation, - particularly in this country, - would be enormously diminished. Wool as it comes from the sheep is an exceedingly dirty product, full of grease and suint. The process of cleansing preparatory to working consists of opening, burring, washing, scouring and dusting,

and in these operations the wool loses from twenty to eighty per cent in weight. The average loss in weight in domestic wools is sixty per cent. The cost of freight on this extraneous material is an important consideration to the manufacturer as on the above basis of shrinkage it adds one to one and a half times the cost of transportation. Moreover as was stated previously the amount of moisture that the wools take up is dependent mostly on the dirt and grease and not on the fibre. Hence if the wool is scoured early its hygroscopic nature is also done away with.

In general the tendency of manufacturing industries to locate near the source of supply, was what built up the little mills of a century ago in the heart of the wool growing districts. This tendency towards the specialization and subdivision of industries of late years has been nowhere more apparent in wool manufacture than in the establishment of wool scouring plants. In 1890 they were so few in number that the textile directories did not report them nor did the census reports of that year take cognizance of them. At the present time twenty five wool scouring establishments are in operation in the United States, employing a capital of $1,061,123. Their location in most instances seems to be determined by their proximity to the consumer and they are in consequence located in the large shipping centers of the wool growing districts. There are six such establishments in New Mexico, Colorado and Missouri; nine in Massachusetts, Connecticut and New Jersey; six in California (five of

which are in San Francisco); two in Illinois; one in Oregon; and one in Pennsylvania. #

Having noted the primary advantages let us now turn to the disadvantages of distinctly local plants.

Firstly, the present method of scouring necessitates a very large outlay of capital in even medium sized plants. Such capital in local districts where the product is uncertain is always at a disadvantage for it is apt at any time, to be made idle.

Secondly, there exists the disadvantage of the great cost of chemicals, (such as lye and soap), which cost, any place outside of the immense commercial centers is very largely augmented.

Thirdly, there exists the difficulty in obtaining competent men for small local establishments where few or no opportunities present themselves. One can readily understand that for such a delicate process as the washing of animal fibre with lye and soap in hot solutions the most higly trained talent is absolutely essential.

The importance of the advantages of local plants would readily impress themselves on one - a sufficient consideration of the dis-

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Twelfth U. S. Census Reports.

advantages would be apt to discourage the most courageous investor.

Why not then obviate the difficulties? How should one set about this? Change the process of washing! And in so doing, do away with: - Firstly, Complicated machinery; Secondly, Expensive chemicals, which cannot be regained in the process of washing; Thirdly, Simplify the process so as not to need skilled labor.

It will be seen that all processes are primarily dependent on the chemicals used in it.

Let us consider the object of the chemicals used in the soda-lye and soap process of washing. - We will describe the process briefly from the beginning. - The raw wools are brought into the upper floors of the scouring plant and after being picked over and "sorted" are placed directly in a "duster", a machine which frees the wool from loosely adhering dust and dirt. A large quantity of dirt still remains, however, matted in with the wool grease. By treatment in a hot water solution (60° C.) of soda-ash, the grease is largely saponified and dissolved away, and the dirt contained is washed off by long continued agitation in warm water. The remaining grease is taken out by washing the wool in a solution of soap. The wool is then washed in several changes of hot water. All this is done consecutively in tanks so arranged with "stirrers", "carriers", etc, that the wool is handled entirely mechanically. After washing it is spread out on screens and dried by currents of hot air. The wool still contains, however, all kinds of leaves, seeds and burrs,

entangled in the fibre. These are removed by treatment with dilute sulphuric acid in a process known as "carbonizing".

The first steps made toward any improvement on the alkali process were made in attempts to regain the fats which had previously been allowed to run off with the waste waters, without being utilized - except to contaminate the rivers and creeks to the detriment of the public health and loss to the public purse.

The scouring plants of Germany and England were the first to install practical methods for the recovery of valuable products from the waste liquors.

There were a number of important patents taken out in England, particualarly, some of the more notable of which are the following:

Improvements in Washing Wools and in Treating and Utilizing the Washings - H. N. Langbeck, Loughton. Eng. Pat. 66. Jan. 2, 1889.-

An Improved Process for recovering Grease from Wool Washing. - P. A. Oliver and V. G. Seagrove. Eng. Pat. 5482. April 10, 1890.

Improvements in Wool Scouring and Fat Saving Apparatus - J. Rhodes, Sidney, Australia. Eng. Pat. 19071. Oct. 24, 1892.

Improvement in Scouring and Degreasing Apparatus.- F. N. Turney, Eng. Pat. 8179, Apr. 22, 1893. Etc. etc.

In 1897 the Bradford district presented a bill before the English Parliament relating to the treatment and disposal of suds from the wool wash-bowls in combing sheds. At that time considerable

interest was attached to a process which had been introduced at the works of Messrs. William Scaife & Co., woolcombers, Laisterdyke. The process was quite successful and exceedingly simple. The suds, after being run off from the washing bowls were allowed to stand for about half an hour in a settling tank, to permit the sand and solid matter to fall to the bottom. The liquor was then pumped into a tank, in the bottom of which was a system of pipes through which compressed air was forced. About one gallon of sulphuric acid was added to every 700 gallons of suds before the "blowing" began. The violent aeration of the liquor brought the grease to the surface very quickly in the form of a thick foam or froth, and a set of boards carried on an endless chain scraped this off and carried it away over one end of the tank. The blowing was continued until all the grease was removed. The greasy foam which contains only about five per cent of water is treated under pressure in a steam press. #

At the works of Thomas Biggart, Ayrshire, England, the recovery of grease and potash from the wash liquor is effected in the following manner:

The suds from the first scouring bowl, containing about nine-tenths of the grease and potash, after standing about twelve hours to insure deposition of the sand are evaporated in a pan until the liquid attains a syrupy consistency. The resulting liquid is then cooled in

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Public Health Journal, 1897.

shallow iron trays, and the grease which collects on top is removed at intervals. The semi-liquid residue is then calcined in a brick oven and the heat produced from it is used to assist the evaporation. A crude carbonate of potash is thus produced, which, after being completely carbonated, is boiled to dissolve out the potash salts. The solution is then concentrated to 100° Tw., the potassium sulphate and chloride crystallizing out on cooling.

Emile Richard-Lagerie of Roubaix, France, has a somewhat similar process, mainly utilized for the recovery of the potash.

Alfred Matte & Co., of the same city have a mechanical process of "battage" for the extraction of the grease from the suds. The suds are beaten into a froth by means of a rotary agitator which carries the fatty matters to the surface. These are skimmed off into conduits by a mechanical scraper and are forced by a steam extractor into a wooden tank in which they are heated to 60° C., and treated with sulphuric acid in the proposition of one pound to 100 gallons. The acid is then removed by washing and the grease is filter-pressed.

In another English establishment that of Thomas Fox, Wellington, Somerset, the soapy liquor are led into six acidifying tanks and treated with sufficient acid to liberate the fatty acids. These, on separating, together with the wool-fat are drained on saw-dust filters. They are afterwards taken off and purified by distillation for conversion into soap again. The dilute acid from the acidifying tanks is pumped into intermediate storage tanks for further settlement, after which it flows

into the precipitation tanks and is treated with the general waste waters from the works by alumino ferric-sulphate and lime. #

This process is somewhat similar to that for the recovery of the so-called "Yorkshire fat" in Yorkshire, England, - a full description of which will be given later.

So much for the methods of recovery of the waste products from the wash waters of the soda-lye and soap process. The process itself is essentially the same as that which has been in use for the last two thousand years, - of course, of late years since the installation of machinery in every branch of manufacture many improvements have been made in the mechanical handling of the wool, but the process itself has remained the same.

It was not until about ten years ago that attention was first drawn to the fact that the old process was inadequate and insufficient to modern necessities and was moreover injurious to the fibre. It was soon pointed out that the ideal process for cleansing the wool and preparing it for dyeing and spinning was the solvent process. All scientists and technical experts who have studied the wool fibre are unanimous in the opinion that it should be freed from its fat by means of volatile solvents and not by the use of soapy and alkaline solutions as has been heretofore the universal practice.

Journal Society of Chem. Industry. Vol. 15, p.47.

To quote from H. G. Kittredge # : "The earlier attempts to carry on the process of degreasing wool by means of volatile solvents were none of them successful from a commercial standpoint, although the rationality of the process was fully demonstrated in almost every instance by the superior condition of the wool thus treated. The problem was a very complex one to solve, requiring considerable mechanical engineering skill, knowledge of the wool fibre and of chemistry,- due regard for the healthfulness and safety of the operation, and a blending of all these requisites into a system, the result of which could be expressed in dollars and cents."

The first attempts toward the application of the solvent process were in the use of carbon-bisulphide, amyl-alcohol and ether as solvents. None of these chemicals proved satisfactory.

Carbon bisulphide had its disadvantage in being difficult to regain without injury to the wool fibre. The use of dry hot air for the removal of the carbon bisulphide made the wool hard and steam felted it. A combination of the two moist hot air seemed to serve the purpose best. There were however many other objections, the difficulty of handling, inflammability, the cost and a tendency to discolor the wool.

Amyl-alcohol was practically out of the question because of the

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Census Bulletin #190, June 16, 1902.

difficulty of obtaining it, moreover the loss of the solvent was too large. Richter of Berlin was the man who attempted this process.

Latere German by the name of Braun claimed to have overcome most of the difficulties of the extraction process in the perfection of an ether extraction apparatus. The process was as follows: "After a portion of the suint and dirt was removed by water, the latter is removed by alcohol, the alcohol by ether, the fat by more ether - the ether by alcohol and the alcohol by water again". Of course the alcohol, ether and fat are recovered by redistillation. The loss of ether did not, it was claimed, exceed one per cent but no statement was made whether it was a loss of one per cent per gallon, per day, month or year. The process nevertheless was a failure. It was certainly not practically feasible and economical on a large scale; moreover it possessed three radical disadvantages, first, a considerable outlay in capital and expensive machinery; second, extremely expensive and dangerous chemicals; third, considerable skill in handling.

Numerous other methods were attempted but none of them were successful. So in the autumn of 1901 the author attempted to devise a method which might do away with all objections and disadvantages.

The first point to be decided upon was a solvent. There are quite a number from which to choose: carbon bisulphide, various al-

cohols, ether, shale oil, fused oil, benzine, benzol, gasoline, etc. and various gaseous light distillates such as naphtha, petroleum-ether, etc. After considerable tentative experimentation it was deemed advisable to use a crude oil distillate, boiling between 85° and 90° C. # The advantages which this product possessed were: firstly, its cheapness; secondly, its absolute non-miscibility with water; thirdly, its excellent solvent power; and fourthly, its low boiling point. None of the other solvents had all of these advantages, the one next in the list is a product called "benzol" manufactured by the Barrett Manufacturing Co. of Philadelphia. These people claim that their product has a greater solvent action on fats than any of the petroleum distillates. But even if so it has the remarkable disadvantage of costing half as much again as the product previously mentioned.

The next step in the work was the designing and the construction of the extraction apparatus. The two most important points kept in mind were simplicity and cheapness.

A temporary apparatus was constructed to work out the general arrangement and method, after which a more complete working model

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(The product which was used in the work was obtained through the courtesy of Mr. Starke of the Standard Oil Company. It was carefully fractionated and then decolorized and deodorized with sulphuric acid.)

was constructed in San Francisco.

The accompanying photographs will convey to one better than a verbal explanation the arrangement of the apparatus. The Blue prints were made from photographic reproductions of the drawings which were submitted in the patent applications.

First Test Machine. (View 1.)

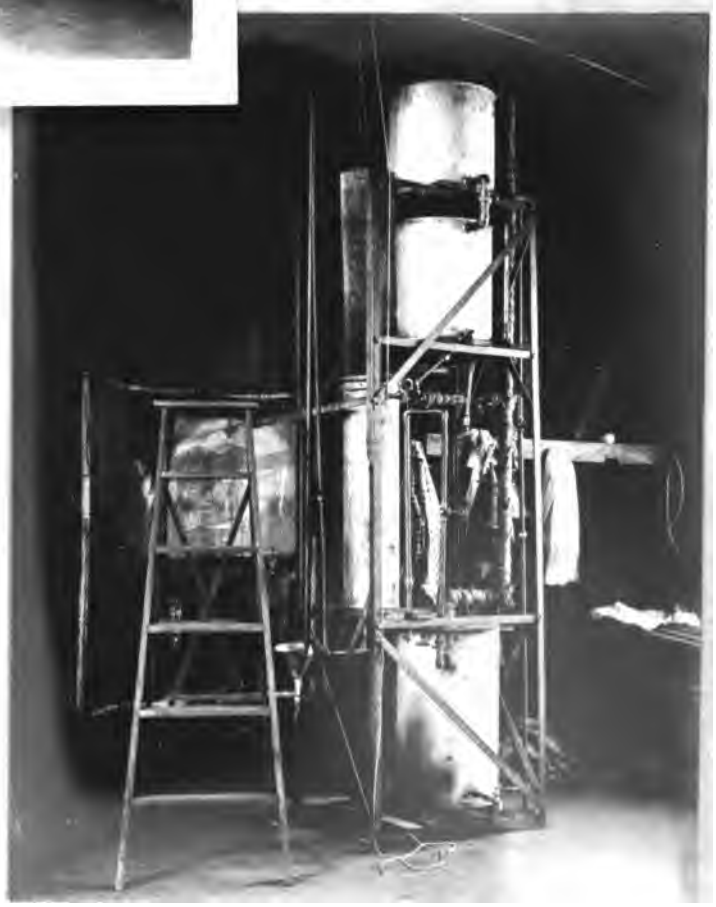
(View 2)

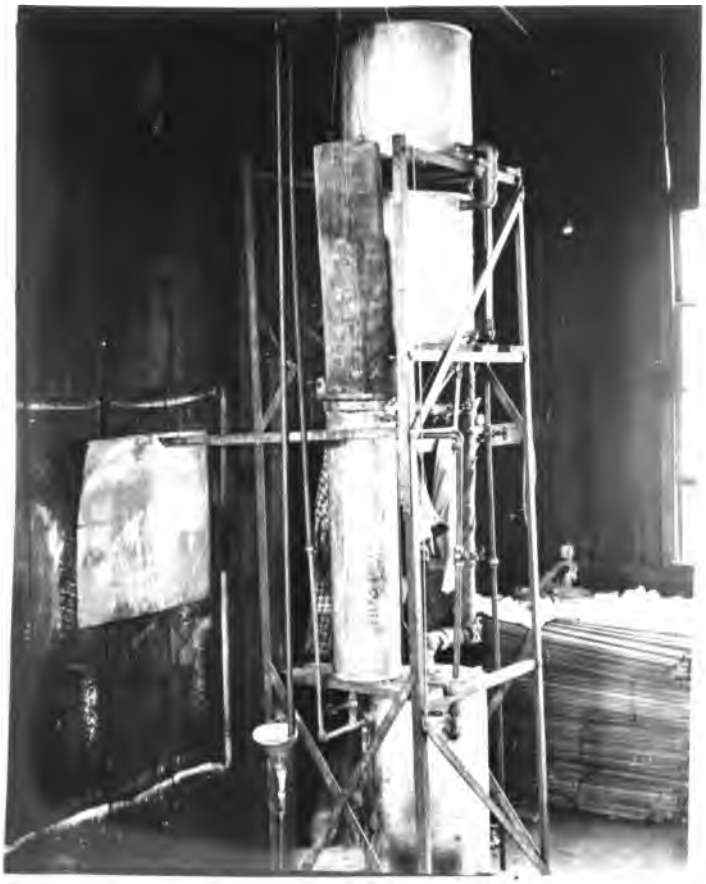
(View 3)

Working Model.

(View 1)

(View 2)





(View 3).

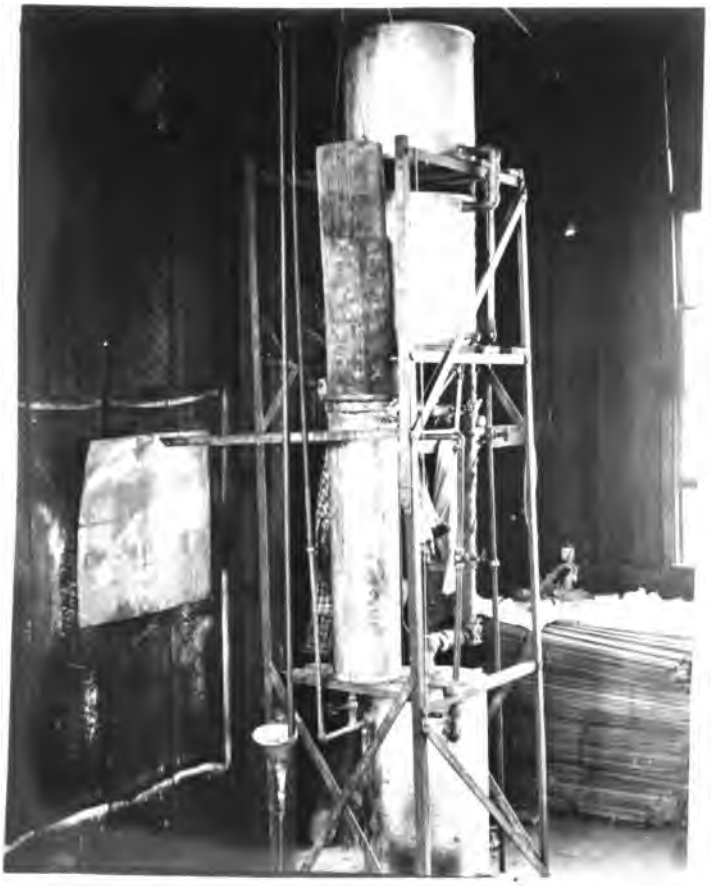
(View 4).

(View 2)

(View 3)

Working Model.
(View 1)

(View 2)



(View 3).

(View 4)

The process consisted in soaking the raw wool in an extractor B (vide Fig. 3) in a suitable solvent. The extractor was a galvanized iron cylinder 9 inches in diameter and 36 inches high, to this there was attached the syphon arrangement E', very much like that in the ordinary Soxhlet extractor except that the attached valves were so arranged that one could extract continuously or intermittently at will. The wool is packed in the wire cage (A). The distillate is allowed to run onto the wool from the reservoir D, and remains in the extractor about twenty minutes. It is then run off into the caldron F. The valves are closed, steam is run through the steam coil G and the distillate is distilled off through the pipe I to the condensor K where the vapor condenses and runs back into the reservoir D to be used over again.

It takes about four separate soakings to remove all of the fat from the wool. After the removal of the fat the distillate is all drawn off into the caldron F and distilled back into the reservoir. The fat remains behind and can be drawn off in the molten condition through the faucet P.

The distillate remaining adhering to the wool is separated therefrom by passing a current of steam through the extractor, the steam and the volatilized distillate condense together and flow back into the reservoir where the water separates on the bottom and can be drawn off at the cock D'.

Upon the removal of the last traces of the distillate the cage is removed, and the remaining dirt and suint in the wool can be washed off by mere agitation in water.

The apparatus is in effect nothing more than a large Soxhlet extractor. It works entirely automatically, the heat of evaporation carrying the distillate to a point where it can be allowed to flow back by gravity, into the extractor. In consequence, from the labor standpoint, the only effort that is required is in charging the wool into the cage and the manipulation of a few valves.

It was shown that it was impossible to damage the fibre by long immersion, for even after standing in the extractor for three weeks the wool came out as strong and tough as when first immersed.

In the first crude apparatus there was a loss of one per cent, of distillate per ten gallons for every five distillations. In the final model there was a barely measurable loss in ten distillations.

It was noted that when the extractor was loosely packed with wool it required about three quarters of a gallon of distillate to every pound of wool.

The extractor cage held from twelve pounds to fifteen pounds of raw wool and from that about three pounds of grease were extracted as a rule. A batch of wool of 75 pounds gave fifteen pounds of grease. The wash waters from the same sample after the grease had been extracted showed an analysis of about six per cent of potash

present (estimated as potassium carbonate).

Most of the samples were absolutely uninjured by the exposure to the steam for ten minutes; some delicate samples were however injured at the "tips" and it was finally decided to do away with the steam entirely by passing water at a temperature of 65° C. into the extractor and then submitting the extractor to diminished pressure. In this way all of the distillate can be recovered at a temperature of 65° and 20 mm pressure. The diminished pressure is obtained by putting a "Deane Simplex Vacuum Pump" in "series" with the pipe O, (fig. 3).

The saving that would be effected by the solvent process to establishments that degrease and work their own wool for worsted purposes can be expressed in round numbers as averaging two cents per pound, figured on the greasy wool - according to H. G. Kittredge. This saving is made: firstly, in the cost of the soap, which is entirely dispensed with by this process; secondly, in a greater yield of the wool fibre since none of it is dissolved by soap and alkali; thirdly, in a larger proportion of "top" to " noil ", because the wool being free from any felting cards, and combs freely without breaking off the fibres or the making of "nibs"; fourthly, in a larger production on cards, combs, drawing and spinning machinery; fifthly, in the superior softness and appearance of the finished

product; sixthly, and perhaps most important of all, in the wool fat and the potash recovered. The cost of the degreasing operation including labor, solvent, power, interest, etc. would be more than covered by the soap saved.

In further consideration of the sixth advantage just enumerated it might be well to call attention to the fact that out of such wools as are worked in the United States, an average of fifteen per cent of fat can be recovered by the solvent process, which at a minimum price of three cents a pound, (Vide Part III. Degras), would bring 45 cents for every hundred pounds of wool degreased, and if to this is added also the value of the carbonate of potash recovered from the rinsing waters, which on an average would amount to 25 cents, net, per one hundred pounds of raw-wool treated, we would have 70 cents as the average minimum value of the by-products recovered from every one hundred pounds of raw wool or seven tenths of a cent per pound of raw-wool treated. Hence it seems safe to say that from two to three million dollars worth of wool fat and potash are run down the streams and wasted annually in the United States, alone. If this wool fat instead of being wasted were recovered and refined and separated into its constituent parts its value would increase at least five fold, and its uses would be sure to multiply.

More progress has been made in the United States in attempts at the practical employment of the solvent process than in any other

country. Plants have recently been erected in Belgium and Saxony but not on so large a scale as in this country. The chief opposition to them must be the revulsion of manufacturers to the giving up of old methods. Though it has been argued that the first cost in the erection of a suitable plant for the employment of the solvent process is a serious obstacle. This can hardly be the case for actual calculations were made on designs and plans, by the author, for a plant of a capacity of 2000 pounds daily. Such a plant would cost about $3500. at the utmost for the solvent process, while by the old method it would cost between $8000. and $12000.

It was the author's intention to start a plant for the degreasing of wool. But information was obtained a short while ago through correspondents in Boston, that such a plant is already in operation in Lawrence, Mass. The Arlington Mills have installed a solvent process and claim that it is quite successful. They are contemplating increasing their capacity fourfold.

As was stated in the preface of this part of the subject, Edward Maertens of Providence, Rhode Island, has patented nearly every available part of the process. (Vide U.S. Patents, April 22, 1902. Patents 698,207 - 8 - 9 - 10 - 11.)

An attempt at the solvent process was made in England as early as 1895 (Eng. Pat. 20,433, October 29, 1895) in which "the wool is treated with a heavy petroleum oil (specific gravity, 0.837 to 0.878) at a temperature of 120° F. On cooling the resultant liquid

to about 70° F. the cholesterol of the suint separates out as a heavy deposit, while the glycerides remain in solution. This solution is found to be an efficient agent in scouring the wool, leaving it in a condition suitable for the subsequent carding, etc. The wool is treated with the petroleum oil in an ordinary wool scouring bowl fitted with pressure rollers. One half to one gallon of solvent is employed for each pound of wool. After about twenty minutes' action the greater part of the liquid is drawn off, and the operation is repeated if necessary. The wool is then treated with water or neutral soap, rinsed, pressed and dried. After filtration the liquid is cooled and the deposit is removed and the clear solution used again. This solution may also be employed as a lubricant or for use on leather, and since it contains no free fatty acids, it would seem to be better adapted for either purpose than the analagous mixture of degras and petroleum oil". No explanation is given as to how the wool is freed from the heavy oil.

The freighting expenses from some wool producing districts to the mills or wool stores are often as high as two cents per pound, and average more than one cent per pound for that part of the clip which is consumed in the eastern and Middle States, and as the average shrinkage of the wool clip is 60 per cent, and some wools shrink as high as 80 per cent, it will readily be seen that in some cases these freight charges amount to ten cents per pound on the clean wool. By establishing degreasing plants at the principal

western shipping points millions of dollars worth of wool, fat and potash could be recovered annually, and from sixty to eighty per cent of the freight charges, amounting to several million dollars more could also be saved. Such a plan, if it were feasible, would have the further advantage of putting the wool upon the market absolutely clean free from further shrinkage, and in the most perfect condition for working. Though, having wool cleaned at the shipping points, some system of grading or sorting the wool according to its qualities would necessarily have to be established in order to meet the requirements of manufacturing.

B I B L I O G R A P H Y .

Blount & Bloxam - Chemistry for Manufacturers.

Brant - Animal and Vegetable Fats and Oils.

Bulletins National Association of Wool Manufacturers.

Journals of the American Chemical Society.

Journals of the Society for Chemical Industry. Vol. I - XX.

Kittredge - Wastes and By-Products (Census Bulletin 190 June 16, 190[illegible])

Muspatt - Technoglogische Chimie.

Sadtler - Industrial Organic Chemistry.

U. S. Patent Office Gazette.

[illegible]

PART III.

THE BY-PRODUCTS OF WOOL WASHING.

(The following work and investigations were carried on, mainly during the period between August and December 1902, in the laboratories of the Chemistry Department, of the University of California. For the reference matter nearly all of the libraies around the bay were consulted.)

Raw wool consists of, firstly, woolfibre; secondly, mechanically adhering impurities, as dirt, burs, seeds, etc., thirdly, natural encrusting matters which come under the techinal heading of "yolk".

Of these the fibre is, of course, the essential constituent, the two other portions constitute the by-products.

The dirt consist mainly of nitrogenous matter and some potash and phosphates. These are very frequently in a suitable condition to be returned to the soil from which they were originally derived. Their value as fertilizing agents seems, however, to have been almost wholly ignored in the past.

The "yolk" is a very important by-product. It is two-fold

in character and consists of the wool prespiration, or suint, which is soluble in water and the wool fat or grease which is soluble in ether.

The suint or sweat is, no doubt, derived from the soil of the pastures, upon which the sheep feed, - which contains considerable portions of potash in the various forms of plant growth. The potash after circulating through the system of the animals is excreted with other matter from the skin and becomes attached to the wool.

The sweat consists essentially of the potassium salts, of oleic and stearic acids, and possibly other fixed fatty acids, also potassium salts of volatile acids like acetic and valerianic and small quantities of chlorides, phosphates, and sulphates. #
(c. f. E. Schulze, Jour. für Prakt. Chimie Vol. 108 pp. 194-203).

It has been supposed by numerous investigators that the combinations in which the potassium is found in the suint as potassium soaps is due merely to the saponification of the potassium carbonate, excreted in a comparatively pure form in the sweat, and saponified with the fats slowly by the aid of normal heat and light.

Formerly the entire amount of suint was allowed to go to waste, when the wool was cleaned, and even now very little is

Sadler, Indust. Organic Chem. 3rd Ed. page 306.

recovered, though at present there is a disposition to recover the potash and potash salts. In fact, the attempt to recover the potash has been the object of establishing a special industry for converting it into commercial products. A number of these were exhibited at several of the industrial expositions in Europe, and especial mention was first made of them ~~at the Paris Exposition,~~ at the Paris Exposition in 1867, many of them receiving the silver medals.

The potash salts were recovered by evaporating and igniting the wash waters by means of which a crude potassium carbonate was obtained. It is estimated that 2,200,000 pounds of this product have been saved from the waste waters of the mills and scouring establishments of France and Belguim. According to M. Chandelon, 2,200 pounds of raw wool may furnish 300 quarts of yolk-solution, of specific gravity 1.25, having a value of $3.75 while the cost of extraction does not exceed 60 cents. #

The various methods of extracting the potash were described in brief in Part II. Nearly every process of value is fully protected by patents. The most important process is that of Mdme. Richard-Lagerie, Roubaix, France. (vide Eng. Pat. 13,677, July 10, 1894.)

Sadler, Indust. Organic Chem. 3rd Ed. page 310.

We come now to the wool fat, the portion of the yolk which is soluble in ether. This, in brief, consists of several solid alcoholic bodies, cholesterine and isocholesterine and other higher alcohols and combinations of these bodies with several of the fatty acids, as stearic, oleic and palmitic acids, etc. Enough has already been said concerning the general occurrence and preparation of the crude wool fat, se we shall now concentrate our attention on its general properties.

Wool fat falls under the natural classification of waxes. We consider the waxes as distinguished from the fats in that they consist of ethers, of monohydric alcohols with higher molecular weight, whereas the fats are series of ethers, of trihydric alcohols, such as glycerols, etc. Other compounds which come under the same category are, Bee's Wax, Spermaceti, Carnanba Wax, etc.

Wool fat from different wools or even from the same wools at different times of the year differs considerably in its general constants, such as the Melting-point, Specific-gravity, Saponification-equivalent, etc.

These constants have been determined by various people. A comparison of their results together with their extreme values is shown in the table on the following page. The methods used for the determination of these values were those of Archbut in his book on lubricants.

It is to be noted that all the waxes have characteristically low saponification values. Hydrocarbon oils, of course, have none. In consequence great care must be taken to free the wool fat from all traces of the distillate used in the extraction. The waxes even though quite free from hydrocarbon contain considerable quantities of unsaponifiable matters; most fats, however, do not contain a greater amount of unsaponifiable matter than from one to five per cent, (chiefly phytosterol, cholesterol, etc.). Hence the determination of the unsaponifiable matter serves as a method of identifying the sperm oils and the waxes, and serves further as a means of ascertaining their purity and estimating their proportion in mixtures.

The Hübl Iodine value serves the same purpose. In this test,- (the percentage of iodine absorbed by 100 parts of the substance under definite conditions, (Vide Jour. Soc. Chem. Ind. Vol. III, p. 641)) depends upon the fact that oils, fats, etc. consist of variable proportions of saturated and unsaturated compounds. The latter readily unite with the halogens to form addition products, the former do not. By bringing the oil or the fat and the halogen together in solution under conditions which reduce substitution to a minimum, it is found that the amount of halogen absorbed by each kind of fat and oil is very characteristic.

The acetylation of alcohols is of value in the same way,

for when alcohols are treated with acetic anhydride they are converted into acetates (esters), the hydrogen of their hydroxyl group or groups being replaced by the acetyl radicle C_2H_3O . For example the cholesterol in the wool fat should react in the following way:

$$C_{26}H_{43}OH + \begin{matrix} C_2H_3O \\ C_2H_3O \end{matrix}\!\!>\!O = C_{26}H_{43}O \cdot C_2H_3O + C_2H_4O_2$$

Cholesterol	Acetic Anhydride	Cholesterol Acetate	Acetic Acid.

Glycerol $C_3H_5(OH)_3$ would similarly be converted into triacetin $C_3H_5(O.C_2H_3O)_3$. This reaction does not interest us though since no glycerol occurs in the wool fat. It is well to know, though, that hydrocarbons are unacted upon. In the case of the monohydric alcohols like cholesterol the esters formed were crystalline bodies insoluble in water and they are easily washed from acetic acid and weighed.

A table showing the comparative results of the acetylation of the monohydric alcohols is shown on the following page#.

Mention must be made of <u>precautions</u> which are found essentail in the determination of the total amount of unsaponifiable matter in the wool fat. The fat must be heated under pressure with alcoholic soda solution of double normal strength

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From Archbut, "Lubricants and Lubricating Oils".

Wax	Alchol	Formula	Formula of Acetate	Yield of Mixed Acetates per 100 parts of Alcohol (Theory.)	Saponification Value of Acetates per cent. Theory.
Wool Fat	Cholesterol	$C_{26}H_{43}\cdot OH$	$C_{26}H_{43}O:C_2H_3O$	III.29	13.56
Sperm-oil	Cetyl	$C_{16}H_{33}:OH$	$C_{16}H_{33}O:C_2H_3O$	117.35	19.76
" Sperm-oil	Octadecyl	$C_{18}H_{55}\cdot OH$	$C_{18}H_{55}O:C_2H_3O$	115.55	17.09
Bees-wax	Ceryl	$C_{27}H_{61}:OH$	$C_{27}H_{61}O:C_2H_3O$	110.61	12.81
Carnauba-wax	Myrcrylic	$C_{31}H_{63}\cdot OH$	$C_{31}H_{63}O:C_2H_3O$	109.59	11.69

Unsaponifiable matter, (mixed alcohols etc.), from	Yield of Mixed Acetates	Saponification Value of Mixed Acetates per cent. (Expt.)
Wool-fat (Crude)	112.21	16.06
" " (Neutral)	112.7	15.63
" " " (Another sample)	108.3	15.32
Sperm-oil	115.71	18.55
Bees-wax	106.46	9.84
" " (Another sample)	107.62	10.25
Carnauba-wax	108.82	12.14
Cholesterol - (Pure)	---------	13.49

for two hours. After the saponification and extraction with ether the formation of a layer of white insoluble flocks between the aqueous and ethereal liquids is characteristic of wool fat and even often, according to some authorities, indicates its presence. Lewkowitsch has shown (Jour. Soc. Chem Ind. Vol. XI, p.134) that these flocks consist of an insoluble soap formed from fatty acids of high molecular weight; they do not belong therefore to the unsaponifiable matter and should be separated from the washed ethereal liquid by filtration through a small dry filter paper.

The Reichert-Meissl Value or the amount of volatile fatty acids present in fats and oils is determined as the number of cc of $N/_{10}$. Alkali required to neutralize 5 grams of the substance. In the case of wool fat it takes 6.5 c.c. of $N/_{10}$ alkali for 5 grams.

The Hehner value, the percentage of insoluble fatty acids contained in an oil or fat is in most vegetable and terrestrial oils and fats about 95.7 except wool fat where it is necessarily much lower.

So much for the numerical constants of the wool fat. In appearance it is sticky and gummy and higly refractive. Its color varies from almost a straw yellow to an opaque amber brown - and sometimes black. It has a very distinctive and disagreeable odor, and possesses a very unpleasant soapy taste.

The compounds derived from it and the uses to which it can be put will be mentioned later - we will first turn to the analysis of the fat.

The first attempts made at an analysis of the wool fat were made by Chevreul. He believed himself capable of distinguishing two different substances in the fat.

1. Very difficulty soluble in alcohol which he called Stearerin, which melted at 60°C and could not be saponified with a water solution of potash.

2. A fatty substance easily soluble in alcohol which he called Elaierin, melting at 15° and saponifiable. He does not distinguish further however even any of the products obtained by saponification.

Hartman was the next to take up the subject, at Gottingen in 1868. He noted that the wool fat contained no glycerols, but did not attempt to point out what alcohols were contained in its place. Later he boiled the fat with an alcoholic solution of potash in a reflux condensor until he had a clear solution.

This solution was treated with a solution of Barium-chloride and the fatty acids were precipitated. Out of the filtrate from the precipitated Barium soaps there appeared a crystalline substance which yielded the identical color reactions of cholesterine determined by Hoppe-Seyler. However, it differed from it in

its outward appearance and had a different melting point. By re-crystallization etc., he obtained a substance which differed from cholesterine very noticably in its composition and yet gave the cholesterine reactions very intensely. He concluded that the fat was a combination of cholesterol with fatty acids, but did not attempt to identify any of them. Hartman's work did not take him much further.

Four years later Schulze took up the problem and his researches on the subject are apparently classic. His first work was devoted to the careful analysis of the suint and then later he took up his work on the fat proper. His work did not come under the authors attention until the early part of November, - had it done so sooner it would have saved an immense amount of unnecessary work. Most of the authors elementary examinations were almost precisely the same and were carried out in much the same way as Schulze's. For example, the first hint that one gets as to how to separate the fats is in noting that the wool fat is only partially saponified by K O H, and that no glycerine is formed. Hence the first step is to separate out the saponifiable from the unsaponifiable matter. Complete saponification is assured by heating under pressure for twenty hours at a temperature of 100° C. The soaps are extracted with water and the alcohols with ether. On boiling off the ether from the second portion one

can fractionally crystallize from a solution of ether alcohol two isomeric substances, one of which gives the reactions for cholesterine the other that of isocholesterine.

Schulze made a combination of the crystals obtained and found by experiment that the molecular weight and formula corresponds precisely with the theoretical for cholesterine. The formula proves itself to be $C_{26}H_{44}O$.

Another method of separating the constituent fats is by utilizing the feature of the difficulty of the solubility of the fatty acids in alcohol - while the cholesterols are comparatively easily soluble. According to Chevreul, one part of Oleic acid is soluble in only twenty-nine parts of ether while one part of the sodium or potassium salt of the same acid is solved in 100 parts of ether. The salts of Stearic and palmitic acids are entirely insoluble (Gmelin Chimie, Vol. 7, page 1492). Berthelot showed, (Aun. Chimie Phys. Vol. 56, page 60), that of the combinations of cholesterine with fatty acids the acetic acid-cholesterine-ether is very difficulty soluble in alcohol, Butyric acid cholesterine ether is very difficulty soluble in even ether, - and soluble combinations of cholesterol with the solid fatty acids is very unlikely since they are themselves very insoluble in even boiling alcohol. The author found that from thirty to forty per cent of the wool fat was soluble in alcohol? The

remaining portion can be almost entirely saponified. By repeated recrystillization from ether alcohol the cholesterol from the soluble portion can be obtained quite pure. Considerable difficulty was, however, experienced in freeing the cholesterine from a white flocky substance which had a tendency to come down with it. As a final resort the difficulty was obviated by crystillization from acetone from which solution the flocky substance will crystallize.

The substance is according to Schulze an isomer of cholesterine and isocholesterine, but received no further designation from him.

An unsuccessful attempt was made to separate the cholesterols by dissolving the whole fat in ether and alcohol and then diluting the mixture. The cholesterols are entirely insoluble in water and should be precipitated out. They do come down, but imbedded in a white flocky precipitate which is so dense that it cannot be dealt with successfully.

A better method and one which is invariably successful and does away with the floculent precipitates entirely is to convert the cholesterols into compound esters or benzoates of these bodies, by heating in a closed tube for twenty four hours at a temperature of 200° C. After heating the excess of benzoic acid is gotten rid of by shaking with K_2CO_3. The mixture is then shaken in a flask with ether. The ethereal layer is separated from the watery one and the ether is distilled

off. The remainder is cooked out with a small portion of alcohol, to separate out the uncombined remaining portion of cholesterol, etc. The combined benzoic acid ethers remain behind as a light yellow crystal powder. They are difficultly soluble in alcohol and are only slowly soluble in ether. The cold saturated ether solution is concentrated slowly over H_2SO_4. Two different kinds of crystals appear. One kind small, thick, and rectangular - the other white, loose, fine needles. The latter are easily washed off from the former and then each can be repurified by recrystallization from ether. The plates appear to be benzoic acid - cholesterine - ether - , in other words cholesteryl - benzoate, (Vide Berthelot, Gmelin-Chemie, V. 7, p.1492), and if so are no doubt of the formula $C_{26}H_{43}O - C_7H_5O$. By decomposition with an alcoholic solution of potash they can be decomposed into potassium benzoate and pure cholesterine ($C_{26}H_{44}OH$), the latter crystallizing from alcohol without a flocky precipitate.

Let us pause here for a moment and look into the subject of -

CHOLESTERINE.

Cholesterine was first discovered by Conradi in 1775 in gallstones. Since then it has been found in human bile, in blood and in the brain; in epidermis and in hair; it is also present in various morbid products of the animal body, e.g. cer-

ebral concretions, scirrhous matter of the merocolon, hydropic liquids of the stomach and of the testicles, etc. It is found too in horn and hoofs; in whalebones, tortoise, shell, feathers, and bristles and occurs in smaller quantities in liver oils, (Shark and cod e.g.), and is characteristic of animal oils generally. Its most abundant source is, however, in wool grease, in which it was first detected by Hartman & Schulze. A very similar substance phytosterol, the cholesterol of plants, is found in the unsaponifiable matter of rape and olive oil and in most, if not all of the vegetable seed oils.

Both compounds are colorless and tasteless, they are crystalline bodies with a greasy feel and a high melting pount. They are insoluble in water, sparingly soluble in cold alcohol but easily soluble in hot alcohol, ether and chloroform and are freely soluble in the neutral fats and fatty acids.

Cholesterine crystallizes out of alcohol in thin white nacreous, monoclinic, laminae with a melting pount of 145°. Out of alcohol ether it crystallizes as weak, easily broken, large, rhombic plates. It crystallizes out of ether in prisms. According to Thorpe it sublimes unchanged at 200° but is decomposed at higher temperatures. Richter states that it distills at 360° with scarcely any decomposition, while Beilstein claims that it cannot be distilled at 360° without being destroyed unless the distillation be conducted in a vacuum, - at

higher temperatures it breaks down into C_2H_2, cholesterilen ($C_{26}H_{42}$), products of the series C_nH_{2n} (boiling point 140°), $C_{28}H_{44}$ (boiling point 240°) and other bodies. (For the author's own work on this subject see the latter part of the paper.)

Cholesterine rotates a ray of polarized light to the left. Its specific rotary power being - 27.5° for red and 34.5° for yellow light. Lindenmeyer has made the following determination of the laevogyratory power of cholesterine for the different fixed lines in the spectrum,

B	C	D	E	b	F	G
20.63°	25.54°	31.59°	39.91°	41.92°	48.65°	62.37°

The rotary power of cholesterine serves as a means of quickly estimating its proportion in various oils such as almond oil, cod liver oil, etc., and of distinguishing these oils from others which do not possess the laevorotary power (e.g. poppy, sesame, olive, rape oil, etc.).#

The ease with which cholesterine is decomposed losing its water - to form cholesterilen,

$$C_{26}H_{44}.O - H_2O = C_{26}H_{42},$$

shows that it partakes of the nature of an alcohol; it is in fact homologous with cinnamyl alcohol and its formula may be

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Watts Dict. of Chemistry.

written $C_{26}H_{43}.OH$.# Heated with organic acids as acetic, butyric, benzoic or stearic acids it forms compound esters, e. g.

$$\begin{matrix} C_{18}H_{35}O \\ H \end{matrix}\Big\rangle O + \begin{matrix} C_{26}H_{3} \\ H \end{matrix}\Big\rangle O = \begin{matrix} C_{18}H_{35}O \\ C_{26}H_{43} \end{matrix}\Big\rangle O + H_2O$$

Stearic acid. Cholesterine Stearate of Cholesterine.

This behavior is similar to that of all tertiaty alcohols with organic acids in watery solutions.

TESTS FOR CHOLESTERINE.

The reaction of cholesterine with H_2SO_4 is best exhibited by dissolving a few centigrams of cholesterine in about 2 c. c. of chloroform and then shaking it with its own bulk of strong H_2SO_4 . The chloroform quickly becomes blood red and then cherry red or purple, a color which it retains for several days. A few drops poured into a basin become blue, green, and then yellow. This change seems to be due to traces of moisture, and the original color may be restored by H_2SO_4 . The H_2SO_4 under the chloroform presents a distinct green fluoreseence. When dropped into glacial acetic acid the liguid, in about half an hour becomes violet, or if much diluted rose colored with a green fluorescence

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(Cinnamyl alcohol has the formula C_6H_5. CH. CH_2OH.by the addition of 17 molecules of CH_2 we would obtain $C_{26}H_{44}O$, Cholesterine, hence its homology to cinnamylalcohol.)

and exhibits such a resemblance to the liquid obtained by diluting Pettenkofers' test for bile acids, with glacial acetic acid, that it is often impossible to distinguish them.#

Lewkowitich believes that the green fluorescence is due to the presence of isocholesterine.##

On triturating cholesterine with concentrated sulphuric acid and then adding chloroform the same blood red solution is formed, which on addition of strong HNO_3 becomes violet, then blue and afterwards colorless.

With concentrated H_2SO_4 and a little iodine a solution of cholesterine becomes violet, blue, green and then colorless.

If to a cold solution of cholesterine in acetic anbydride concentrated sulphuric acid be added drop by drop without shaking, a violet coloration, quickly changing to blue, is produced where the liquids meet. On shaking the whole liquid becomes deep blue slowly changing to green or bluish green. This reaction is very delicate and is given by less than one mg. of cholesterine in 2 c. c. of acetic anbydride. Isocholesterine gives the same reaction, (Schulze). A violet coloration is given also by colo-

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British Pharmacopeia.

Hammersten Physiolg. Chem. -

phony and rosin-oil in acetic anhydride but in these cases the color which is produced by one drop of H_2SO_4 and shaking does not change the blue but either fades to a neutral tint or changes to a brown or yellow color.#

With HNO_3, (Schiff). A crystal of cholesterine heated with a drop of concentrated HNO_3 and slowly evaporated leaves a yellow spot which is turned red by NH_4OH. Isocholesterine gives the same reaction.

If a little cholesterine be triturated with a drop of a mixture of three volumes of strong HCl and one volume of Fe_2Cl_6 solution and be slowly evaporated to dryness, the particles which remain undissolved assume a violet red color changing to blue. Some other substances, however, such as turpentine and camphor behave in the same way. Isocholesterine does not give this reaction. (Schiff).

BEHAVIOR WITH REAGENTS.

When strong H_2SO_4 is added gradually to a slightly heated mixture of cholesterine and dilute H_3SO_4, the cholesterine becomes soft and decomposes, giving off all of its oxygen in the form of H_2O, and is changed without evolution of gas into three isomeric hydrocarbons, which Zwenger designates, as cholesterine, A, B and C; - they are insoluble in water and may be freed from

Liebermann. -

H_2SO_4 by washing in H_2O. These hydrocarbons are very easily crystallizable and like cholesterine are remarkable for possessing high melting points. (A) has an earthy aspect and a m. p. of 240° C.,and is only sparingly soluble in ether. (B) forms shining scales melting at 255° , and is moderately soluble in hot ether, (if kept in the fused state it loses its power of crystalizing,) (C) is resinous without appearance of crystalization and melts at 127°, it is also soluble in hot ether.

When cholesteric is treated with HNO_3 in a retort with a reflux condensor - a resinous mass is formed which is slowly dissolved after prolonged boiling with excess of nitric acid. The liquid when sufficiently concentrated in the retort leaves an acid gummy residue containing a large quantity of cholesterine acid and a resinous substance. The residue on cooling separates into two layers, the upper of which consists of crystalizable choloidanic acid, while the lower which is viscid consists chiefly of cholesteric acid containing a little oxalic acid. On saturating this liquid with NH_4OH., and precipitating with $AgNO_3$, and boiling the precipitate with H_2O, cholesterate of silver is deposited.in crystalline crusts, which when decomposed by sulphuretted hydrogen yield cholesteric acid. This acid is a yellowish gummy solid resembling the gum of the cherry-tree. It is deliquescent; very siluble in H_2O and alcohol; has an acid, bitter, astringent taste and is decomposed by distilling, giving off

bitter vapors and leaving a considerable quantity of charcoal. The alkaline and earthy salts are uncrystalizable, while the salts of the heavy metals are insoluble. Its formula is supposed to be $C_{26}H_{42}O_4$.#

By oxidation with K_2MnO_4, cholesterine is said to yield three oxyacids. - Cholesteric acid ($C_{26}H_{42}O_4$) oxycholesteric acid ($C_{26}H_{42}O_5$) and dioxycholesteric acid ($C_{26}H_{42}O_6$). These acids are soluble in NH_4OH and form amorphous precipitates with all metals; those of dioxycholesteric acid dissolve in benzine, but are insoluble in alcohol and ether; those of the oxy-acid dissolve in benzine and ether while those of cholesteric acid dissolve in alcohol, ether and benzine. (Latschinoff (Bull. Soc. Chim. (2), XXVII, 456).

Oxidized for twelve hours with H_2SO_4 and $K_2Cr_4O_7$, cholesterine yields a white amorphous acid product having the composition of oxycholic acid $C_{23}H_{40}O_6$ together with small quantities of the lower terms of the fatty acid series (probably acetic propionic and butyric acids).

(L. Henry Ber. d. Deutsch. Chem. Ges. V. 5569).

Cholesterine resists the action of concentrated alkaline solutions even at the boiling heat, but lime decomposes it at about 250°C, hydrogen being given off and the cholesterine being

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Watts Dict. of Chem. -

converted into an amorphous fatty body nearly insoluble in alcohol.

With concentrated phosphoric acid, Cholesterine forms two compounds, called cholesterone α and B, isomeric with each other, but differing in their physical properties. Cholesterone α forms very brilliant rectangular prisms melting at 68° C, and distilling almost without alteration easily soluble in alcohol and ether. The modification B forms small silky needles sparingly soluble in ether nearly insoluble in alcohol.

Cholesterine treated with phosphorous perchloride, PCl_5, yields neutral phosphuretted bodies which are difficult to purify, and resemble the so-called myolin group.

(Ann. Chim.. Pharm. CLVII, 284).

Cholesterine is attacked by chlorine and bromine yielding substitution products. The chlorine compounds are $C_{26}H_{36}Cl_8O$, and $C_{26}H_{43}$. Cl. (Beilstein).

The benzoate of cholesterine ($C_{26}H_{43}O \cdot C_7H_5O$) crystallizes in small shining micaceous laminae which melt between 125° - 135° C, it dissolves with moderate facility in ether and is sparingly soluble in boiling alcohol.

The butyrate of cholesterine ($C_{26}H_{43}O \cdot C_4H_7O$) is easily fusible and somewhat soluble in hot alcohol.

The Stearate ($C_{26}H_{43}O \cdot C_{18}H_{35}O$) crystallizes in small shin-

ing needles having a neutral reaction. It is sparingly soluble in cold ether nearly insoluble in even boiling alcohol. (Buttelot).

The acetate ($C_{26}H_{43}O \cdot C_2H_3O_2$) is produced by treating cholesterine with acetyl chloride. It crystallizes in small colorless needles melting at 92° C. (Henry).

Cholesterine Amine ($C_{26}H_{43}O \cdot NH_2$), is prepared from the chloride, ($C_{26}H_{43}Cl$), by digestion with alcoholic ammonia. It crystallizes in small plates melting at 104°. (Henry).

ISOCHOLESTERINE.

It was mentioned previously that the portion of the wool fat which is soluble in alcohol, the unsaponifiable portion, consists almost wholly of two isomeric monohydric alcohols, one cholesterin, the other isocholesterine. These alcohols are separated in the last method mentioned, by conversion into the benzoic esters of these bodies, by which means the cholesterine is obtained in the form of small rectangular plates, the isocholesterine in the form of needle like crystals. These later crystals on decomposition by means of alcoholic potash in a reflux condensor yield potassium benzoate and isocholesterine. This compound Schulze found to have precisely the same formula as cholesterin. From concentrated alcoholic solutions it appears as

a gelatinous mass; from dilute solutions in white flocks. It crystallizes from ether or acetone in fine transparent needles, which on filtering off and drying have a white porous shining lustre. The crystals melt at 137-8°C to a colorless fluidity which on cooling appears as a brittle, glassy, transparent mass. A mixture of cholesterine and isocholesterine is found to melt considerably lower than either compound.

Most of the test reactions are the same as those of cholesterine; it is though distinguished from this substance in the test with H_2SO_4, chloroform and Fe_2Cl_6.

The differences between the three isomeric substances cholesterine, isocholesterine and phytosterine is shown in the following table:-

	Cholesterine	Isocholesterine	Phytosterine.
Point of Fusion ° C.	146°-148° (Bomer)	137°- 138°	135.5° - 141° (Bomer)
Crystalline form.	Thin rhombic plates of $C_{26}H_{40}O.Ag$, from hot alcohol and ether. Anhydrous needles from chloroform.	Flocks from dilute alcohol; a jelly from concentrated alcohol; - needles from ether.	Tufts and needles, $C_{26}H_{44}O.Ag$- from hot alcohol.- Anhydrous needles from ether and chloroform.

According to Bomer these alcohols cannot be separated by crystallization. Lewkowitsch denies this. (Vide Jour. Soc.

Chem. Ind. Vols. IX & XI.) The author's work agrees with that of the latter investigator.

COMPOUNDS OF ISOCHOLESTERINE.

The benzoate is found to melt at 190° - 191° C; is very slightly soluble in alcohol, more soluble in hot acetone and still more easily soluble in ether, from which it separates in microscopic needles. It is an isomer of benzoic-acid-cholesterine-ether.

The acetate is prepared by heating the isocholesterine with acetyl chloride on a reflux condensor until no more H Cl is evolved. The fluid is then shut up in a tube and heated on the water bath for some time. The surplus acetyl chloride is gotten rid of by dilution and the resulting ether is taken up and crystallized out of alcohol. It appears as a white amorphous mass.

Isocholesterine is easily soluble in hot acetic acid which on cooling separates out a compound of isocholesterine and acetic acid, - in a white flocky precipitate which on heating again loses its acetic acid.

Isocholesterin Stearate, was prepared by Berthelot by heating isocholesterine with stearic acid in a closed tube at 200°C. The product melts at 72°C. and has a very fine needle-like powdery appearance. It is only slightly soluble in boiling alcohol, appearing from the cold dilute solution as white

Phosphorous porchloride converts isocholesterine into a yellow-resinous mass easily soluble in ether, slightly soluble in alcohol and having the composition of isocholesterine chloride ($C_{26}H_{43}Cl$.)

There is also a third alcohol present in the soluble portion of the fat. This is shown by the low carbon content of the mass of raw alcohol when decomposed with alcoholic potash. It does not occur in very appreciable quantities and can only be obtained from repeated recrystallization of the mother substance from acetone.

LANOLIN.

The entire saponifiable portion of the wool fat is found in commerce mixed with about thirty per cent of water, under the name of lanoline. Commercially this is the most important product which can be obtained from the raw fat. It commands a price in the wholesale market of from 30c. to 40c. a pound. It is highly prized because of its wonderful medicinal properties. It does not become rancid, is quite antiseptic, and is absorbed by most animal tissues with remarkable avidity. No substance is known of the same nature which has as much resorbtive power; (it will take up 110 per cent of its own weight of water.) It

has been found moreover to "constitute an excellent remedy for cuts and burns. In the case of cuts, especially after a careful annointing with lanolin, scale is never formed, the substance acting according to Fraukel as a preventative. It is noticeable that cuts when protected by an application of lanolin can be cooled in a rapid stream of water without danger of removing the lanolin. Bleeding is arrested almost instantly". #

"In agricultural circles, lanolin has attracted considerable attention on account of its property of preserving the elasticity of hoofs and the suppleness of leather. It owes its superiority in this respect to its ability to mix with water, in consequence of which it penetrates better than any other fats into moist leather and the deep layers of the skin and of the hoof". ##

The better qualities of lanolin are of a yellowish white color and have the consistency of a stiff ointment. It should always have a neutral reaction. It melts at 138°C.

It was first prepared on a commercial scale in Germany in 1882 by Braun and Liebrich, (Jour. Soc. Chem. Ind. Vol. IX p. 356). They described their product as a combination of pure wool fat and water, but the appearance of the preparation show-

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National Dispensatory.

Thorpe, Dict. of Chem. Vol. II, p. 398.

ed that it was far from pure. The color of this anhydrous wool-fat was of a greenish brown, and when mixed with water a dirty yellow, containing still free fatty acids and if kept for some time even in a closed vessel it assumed a brown color on the surface besides retaining the characteristic disagreeable smell of sheep. It was prepared as follows:- "The fresh wash water from the scouring plant are passed into a centrifugal machine in which the dirt and water are separated from the fat. The fat thus obtained constitutes the raw lanolin is kneaded in a stream of cold water until the water which flows away is as clear as the flowing water. The raw lanoline is heated with water whereby it is separated into water and fat and the latter is skimmed off. It is then reworked in a centrifugal machine dissolved in ethyl or methyl alcohol for purification. The fat so cleansed is kneaded with water and placed on the market as lanoline.

Another process was patented in England in 1886 by A. W. Langbeck and A. Ristert #, in which raw-wool-fat is treated with boiling alcohol containing about ten per cent of ether, by which means the free fatyy acids, free cholesterine and isocholesterine and the volatile fatty acids present in the wool fat are dissolved out. The remaining cholesterine ethers are then

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Jour. Soc. Chem. Ind. Vol. IX.

treated with steam in order to drive off remnants of the solvent. Or, the raw fat is dissolved in ether and the cholesterine ethers separated by the addition of alcohol. Thus purified they are mixed with about twenty per cent of water and called "cholesterinol". However, wool fat thus purified leaves much to be desired as the presence of waklike cholesterine ethers of higher melting point render it tough and brittle and make it unfit for pharmaceutical purposes. Patents were later taken out by the same men by which the raw fat was worked by separating the free fatty acids by means of a solvent, such as alcohol mixed either with chloroform, CS_2, acetone, benzoline or naphtha or by distilling off the fatty acids, preferably by superheated steam at a temperature of 400°- 450°F. The fatty residue after the separation of the fatty acids, is then filtered through animal charcoal, (especially that known as prussiate waste), either by maintaining the fatty matter in a fluid condition, by heat applied to it and to the filter or by first dissolving in benzoline, CS_2 or acetone and filtering the solution. The solvent is then recovered by distillation and steam or warm air is blown through the fatty matter until all traces of the solvent disappear. The so purified fat is anhydrous, of a yellow color and free from smell; if required as a basis for ointments, pomatums, etc., it is mixed with from

twenty to thirty per cent of either water or H_2O_2. The material then produced is pure white.

A. von Rad of Bavaria, Germany, patented a process in 1887, in which he utilized the lyes from washing works. These are precipitated with slaked lime and deodorized with chlorinated lime or permanganate of sodium or potassium. The precipitate is then dissolved out successively by alcohol benzine, CS_2, benzol and a mixture of ether and chloroform, and in order to give the fats a proper consistency he mixes with them a neutral ethyl or methyl ester of oleic acid and calls it "Lanesine". Later on he obtained a second patent by which he treats the raw fat with alcohol and sulphuric acid thereby changing the free fatty acids into the corresponding esters.

A process was patented in France by C. Baron (Rev. Chim. Ind. 1897, VII, p. 111) whereby 800 kilos of crude grease are placed in an auto-clave with 100 litres of NaOH, (3.25°B), and boiled with live steam for three hours at a pressure of two atmospheres. 200 kilos of water and 300 of acetic ether are next introduced and the agitation is continued for eight hours at a pressure of four atmospheres. The whole is then allowed to rest until the liquids separate. The ethereal layer is drawn off and washed with water which is at first made slightly alkaline and then warmed to 60°. It is finally filtered and the acetic ether distilled off. The residue is sold as lano-

line. The aqueous liquid is decomposed with sulphuric acid and the fatty acids are washed and made into soaps.

RECOVERY OF SOAPS FROM WOOL FAT.

The idea was long ago conceived of separating the fatty acids contained in the grease and rendering them suitable for the manufacture of soap.

Buisine was the first to attempt a process on a large scale. (Ber. d. Deu. Chem. Ges. 1885 Refer. 5467). He heated lime with the fat, under a pressure of eight atmospheres, then the cholesterines were distilled off with superheated steam and the nonsaponifiable admixtures were extracted by means of a solvent. From the lime soap remaining behind the fatty acids were obtained by the addition of hydrochloric acid. The viscous slime obtained from the wash waters by precipitation with line were used in the same way.

Later Violette working at the same establishment as Buisine, in Lille, took out a patent on the following process, (Ger. Pat. 32015 Oct. 25, 1889). The dried wool fat is heated with solid alkali at a temperature of about 300°C., the air being excluded, for which purpose superheated steam or an indifferent gas is conducted through the apparatus. In this reaction the fatty acids are no doubt fixed without alteration as alkaline

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soaps, after which the alkali acts at a sufficiently high temperature upon the neutral esters to decompose them into their constituents; namely oleic, stearic, cerotic acids etc., (which are readily fixed as soda soaps.), and to alcohol cerylic alcohols cholesterine, isocholesterine, etc. The soaps are dissolved out of the mass by means of water out of which they crystallize on cooling. They are then decomposed directly or through transposition with acids into potassium soaps. There results a mixture of fat and oleic acids which are separated by means of fractional distillation and filter presses.

In Yorkshire, England, the fats resulting from the soap suds and other waste liquors are regained and utilized in the soap industry. The method of recovery is as follows:- The soap suds and waste liquors are conducted into large tanks, holding from six to eight thousand gallons, and acidulated with H_2SO_4 or HCl. After standing for some hours a fatty mass, the so-called magma, separates out and deposits on the bottom of the tank. This is thrown on filter beds, pressure and heat applied and the product obtained, a sticky grease of a brown to black color is the "Yorkshire fat". This is sometimes used in the manufacture of soap, for oiling and for other lubricating purposes. It is, though, most frequently subjected to distillation with superheated steam, which process yields "spirit oil, grease, green oil, pitch, water, etc." The first distilled

[illegible]

grease is seeded with oelin and filtered and pressed. "This olein with soda forms an extraordinary gelatinous soap from which free oil cannot be extracted even with ether." Another product is obtained by adding 25 per cent paraffine, which makes a valuable leather dressing.

One of the Glasgow wool mills took out a patent in 1893 # which covers a process for separating soap and lanoline by adding to 100 parts of the grease, - contained in a vessel heated by steam a solution of potassium bicarbonate or borax of about 8° Tw. (300 parts) and boiling for six hours. After settling the vessel is heated by direct fire and a solution of NaOH (25 parts) added at a strength of 30° Tw and the mixture is boiled for three hours. The suint rises to the surface as a thick pasty scum, as soon as the fire is drawn, while underneath it, remains a pure, dark colored olein soap which by boiling down and the addition of small quantities of KOH (35°Tw) and mixing with pale soap (5 parts) and cocoanut oil soap (2-1/2 parts) or olive oil (5 parts) is converted into a marketable product.

Messrs. Jaffe and Darmstadter patented a process in which the constituents are separated by emulsification with vegetable fibres, saponine or drugs containing pancreatine. The soaps are then precipitated with salts of the alkaline earths

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(Jour. Soc. Chem. Ind. Vol. XII.)

or the heavy metals and extracted with solvents. This method does not, however, seem practicable since the emulsified wool fat forms, when stirred or shaken with any of these solvents, a jelly which it is almost impossible to separate.

Recovered soap is in itself unfit for washing purposes because it contains a large amount of soap which does not give a good lather with water. It contains besides a small quantity of cholesterine ethers of a high melting point. Since the raw fat is unsuitable for giving a hard soap it might be advisable to separate those soaps which are insoluble in cold dilute spirit by filtering from those soluble in that medium and use them not by themselves but in addition to soap. In that way a hard soap would be obtained.

The soap remaining on the filter after saponification of the raw fat is insoluble in water but is soluble in hot alkali. If it is filtered cold through flannel bags; the filtered liquid can be recovered by distilling off the solvent. Whilst the remnant on the filters can be made use of, after decomposition with acids for the manufacture of candles.

A property of the wool fat that has not yet been technically utilized in the attempts to manufacture soap from it, - is its capability of absorbing large quantities of sulphuretted hydrogen and combining with it. After saturation the fat readily saponifies with soda at low temperatures, carbonic acid being evolved. Saponification may also be effected directly

with alkaline sulphides without the evolution of H_2S. By this process a product is obtained which, according to Borchers, "deviates completely from the properties of its constituents and may be considered a true soap". The sulphur soap thus obtained yields but little lather and has a slightly disagreeable odor. These soaps like so many of the other sulphur soaps may be used as a remedial agent in skin diseases, otherwise they would possess no distinctive advantages over other soaps of the same nature.

OTHER METHODS FOR SEPARATING THE CONSTITUENTS OF THE WOOL FAT.

Lanichol, a product described in a Canadian patent is prepared by separating impurities of an albuminous gummy or similar character from the fat by boiling nine parts of wool grease with as much resinate of soda, (made by boiling together rosin and twice its weight of soda crystals), as contains one part of rosin. Brine is added and the whole boiled up with steam, enough salt being added to prevent thr whole of the grease from going into solution. The undissolved grease is boiled up repeatedly with brine to wash out impurities and finally with water containing alkali in solution. Free fatty acids dissolved in the grease are washed out. On standing "lanichol" rises to the surface, whilst good soap stock is obtained on treating the soapy wash waters with salt.

L. Darmstadter claims to have isolated several new acids from saponified wool fat. (Jour. Soc. Chem. Ind. Vol. XV). He says: on saponifying wool fat and extracting the saponified substance with petroleum ether and then with alcohol, a new acid, lanocerinic acid, ($C_{30}H_{60}O_4$), is botained. This acid loses water to form the anhydride ($C_{30}H_{58}O_3$). The anhydride breaks down to form a lactonic decomposition product, $C_{10}H_{20}O$, this substance is identical with menthol. The residual soap is dissolved in dilute alcohol and carefully decomposed with dilute HCl. The lanocerinic acid is almost insoluble in H_2O and cold alcohol, but it is easily soluble in hot alcohol from which it crystallizes as small plates (m.p. 104°- 5°C.) . The extract from the above mentioned soap consists of three alcohols, one of which has been indentified as cholesterol.

Lewkowitsch dehydrated the wool fat by melting and allowing the water to subside. The anhydrous fat was then dissolved in absolute alcohol by means of metallic sodium in a reflux condensor. The alcohol was distilled off and the fat shaken up with ether and water. (1). The ethereal layer on the top seemed to consist of an ethereal solution of the alcohols, the unsaponifiable matter. (2). The agueous layer on the bottom being a solution of soap. (3) An intermediate thick layer representing a soap sparingly soluble in water. The same investigator claims that the cholesterols can always be readily separated

from those of the aliphatic series because of the behaviour of the latter towards soda lime when they are converted into the corresponding fatty acids.

Newmeister claims that one of the best solvents for separating cholesterine from the fatty acids is acet-acetic-acid - ettyl-ester. Cholesterine is quite soluble in it while the fatty acids are not.

A. Buisine claims (Compte Rendu Vol. 134, p. 66), to have isolated the following substances from the wool grease: "Carbon-dioxide, ammonia, and potassium carbonate, - acetic, propionic, butyric, baldrianic, caprionic and cerotic acids all united with potassium. Further he claimed to have found phenol (as phenol sulphuric acid), lactic, benzoic, oxalic, succinic and uric acids: - glycocol, leucin, tyrosin and similar dye stuffs. The substances named were all found in notable quantities. Suint of an Australian wool had for example in 100 parts, remainder, 7.1 portions of acetic acid, 4 parts of propionic acid, 2.6 parts benzoic acid, 2.5 parts lactic acid and 1 part of caprioic acid." These statements certainly seem very bold. Perhaps the occurrence of phenol, benzoic acid, etc., could be accounted for by the wool having been emersed in sheep dip.

There is a patent out covering the simple methods already brought forward, by the means of which the fat is separated

into its constituents by boiling in solvents only. By this means the fat is separated into three primary and two secondary products by means of acetone-alcoholand alcohol-acetone. By dissolving in acetone-alcohol products designated as #4, 1 and 3 are obtained. The fat is then digested in hot acetone and cooled until the solution is saturated with the product #5.- It is then decanted off and #5 is recovered by distilling off the acetone. The same process is then gone through with alcohol and #1 is produced. The fat remaining is called #3. The #4 product is the residue after the removal of #5. The alcohol-acetone process consists in mixing alcohol with the raw fat. #1 goes into solution, the remaining substance is #2, which is a mixture of #3 and #4. After freeing from alcohol and incorporating with cold acetone #3 goes into solution and #4 remains behind. #1 is a transparent fluid or semi-fluid of a yellowish red color, inodorous , and soluble in cold acetone and cold alcohol. It is composed of fatty esters and resinous gummy matters. When dissolved in 76°B naphtha, the resinous matter precipitates on standing. #2 is a mixture of #3 and #4. #3 is an oily opaque fluid or semi-fluid solid, inodorus, and soluble in cold alcohol. It consists of a mixture of esters of isocholesterine and allied bodies. #4 is an opaque solid and inodorous, waxy, fatty matter of a whitish color and consists of a mixture of esters or fats of cholesterine, insoluble

or but slightly soluble in cold or hot alcohol and cold acetone, but quite soluble in 30 times its volume of boiling acetone.

The author had adopted a method in the early part of the investigations similar to that just described. The separated grease was, however, first purified by dissolving in petroleum-ether and allowing the dirt to settle. The solution was then decanted and the solvent distilled off, after which the fat was separated into its constituents by dissolving in acetone and alcohol. Another method used with some success by the author was to dissolve the fat in a crude oil distillate of about 55° B. The solution was then concentrated by distilling the oil under diminished pressure, and was then cooled. The cholesteryl bodies are the first to crystallize out and can be separated by filtration on a flannel. The crystals occur as large coarse needles. They can be readily emulsified with water and be made directly into a fairly good lanoline.

Full details as to the exact methods employed in the rather difficult and certainly troublesome process of refining the crude wool fats are not obtainable from any of the available publications, the brief descriptions given in the various patent specifications form a chaos out of which it is difficult, in fact almost impossible to decide accurately which points are and which are not of actual practical utility.

DESTRUCTIVE DISTILLATION.

On destructive distillation the crude fat can be broken up into a number of oils which distil off, and a pitch (of about the density of "D"asphalt). The oils vary in color from a light straw yellow to a dark amber brown. They all possess a disagreeable odor which very much resembles acrolein. The presence of acrolein can easily be accounted for since the fat was found to contain potassium salts of oleic and stearic acids, and it is a well known fact, that when these acids are heated to a high temperature with salts of the alkali metals, they break down into acrolein and various other products. (Vide, Novy Physiological Chemistry). These oils possess a very marked fluidity even those of the higher boiling points and the latter have a decided fluorescence. This latter characteristic seems to be a property of all hydrocarbon oils. According to Archbutt, "a distinct fluorescence proves the presence of hydrocarbons, though a non-fluorescence does not prove their absence."

The oils on first distillation contain considerable foreign coloring matter which was removed by only one single reagent, glacial acetic acid. Odors are very frequently removed with H_2SO_4 or Na_2CO_3, but these oils seem to be unaffected by these reagents. The "gravities" of the oils ranged from .795 to .817.

The oils from the first distillation were all combined. 50 cc were taken and redistilled. The results are shown in the following table:

Fraction	Taken between (°C.)	Yield	Color	Odor	Remarks.
I	100-120°	12	Straw	Mild	Very fluid and re-
II	200-250°	7	"	"	tain clear color.
III	250-275°	10	Yellow	Acrolein	Non-drying oils did
IV	275-300°	12	"	strong acrolein	not show signs of drying after 8
V	300-350°	5	Dark Yellow	strong acrolein	weeks exposure.
VI	350-over	5	Dark Yellow	not bad	Fluorescent, jelly. Turns dark.

The oils were not acid and hence might be used for lubricating purposes, numbers III, IV and V would serve that purpose particularly well, since they are non-drying.

The pitch that was left behind, can, on extreme distillation be carried to the state of a porous coke. This on analysis seems to consist of potassium carbonate and nitrogenous carbon. A similar product is used in the manufacture of yellow prussiate of potash. This compound might be put to the same purpose.

Other uses to which the crude fat can be put:

Rosengren, a Swedish investigator, claims that he can use the fat to make anhydrous, transparent, homogenous solid pro-

ducts with petroleum. He also uses the fat to increase the consistency of different oils of low viscosity and at the same time raises their melting points to as high as 152° C.

These facts could be made use of in the manufacture of rubberoid roofing. Mr.Finley of the Parraffine Paint Co., tried some of the fat obtained by the author and found that, when mixed with the composition which makes the roofing, it renders it more durable and far more pliable.

Wool grease has been applied in the leather industry for a number of years. Some experiments performed in Europe and described in the Journal of the Society of Chemical Industries (Feb. 28, 1898) are spoken of as follows: "in'stuffing' a number of samples of leather with a mixture of wool grease and tallow, the latter showed that the neutral wool grease penetrated better than any other fats of the same consistency; that it left no sticky touch or oil odor; and that in the case of chrome-tanned leathers especially, it gave a very good color.

Wool grease under the name of "degras" is used very largely for the stuffing of leather. In general the term "degras" is applied to all oils and greases used by tanners without any special distinction, including what is known as "sod oil". Sod oil and wool grease have entirely different constituents as well as characteristics, and hence should be easily distinguished. Wool

grease is extracted from wool; sod oil is extracted from leather which has been curried with oils, particularly fish oils. Sod oil contains a resinous substance (not a resin) known as "degras former", which is characteristic of sod oil. No other oil or grease (not even wool grease which is techinally a wax and not a grease at all) contains the degras former, which is therefore characteristic of sod oil. Originally sod oil only was known as degras. Later the term was made by the American oil trade to embrace wool grease, and was adapted less extensively by the English. #

The author obtained some degras from Balfour Guthrie and Co., of San Francisco. The firm, the largest wholesale commission merchants on the coast, handle thousands of tons of degras every year, which they sell to the leather tanners. The acidity of the samples obtained,lead one to suspect that the fat is recovered from waste wool scourings by treatment with sulphuric acid. (Leather softened with degras of an acid reaction deteriorates rapidly.)

The crude degras commands a price of from four to four and a half cents a pound in the open market. The amount that was imported into the United States for consumptiom in 1899-1900 was

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E. Hopkins, Jour. of the Amer. Chem. Soc. June 1900.

13,263,480 pounds, valued at $286,485 duties paid. (United States Census Reports).

There hardly seems a doubt, but that the recovered grease from the solvent process will in a few years, if the process is developed, wholly displace the crude degras which is at present on the market.

Now that we have considered the composition and possible uses of the bi-product of the wool washing industry, let us glance at a few figures before closing.

The world's annual supply of raw wool amounts to about 2,500,000,000 pounds. Let us see what this would yield. At an average price of 10c. per pound for the raw wool the whole would amount to $250,000,000. Say as much as 35 per cent (a large figure). of the raw wool is recovered as pure fibre; - Considering the scoured wool as the only product, which it is according to the old methods of scouring, it will be seen that a market price of 30 cents a pound for the washed wool would barely compensate for the "shrinkage" and pay for the cost of washing. By the old method of washing 25 per cent, amounting to 625,000,000 pounds of fat, are thrown away annually. Were this fat recovered 25 to 30 per cent of it could readily be separated and converted into lanoline, and the remainder could

be used as soap-stock, axle grease or candles - or be converted by destructive distillation into lubricating or paint oils. Since lanoline has a market value of 35 cents a pound the value of this product alone (estimating the grease to contain as little as 25 per cent) would amount to $54,687,500. If the remainder of the grease were sold as soap or candle stock at say four cents a pound it would bring $18,750,000. income, a year. And omission must not be made of the potash salts, which constitute six per cent of the raw wool. These at five cents a pound would bring $750,000. a year.

It would seem as though it were about time for some one to be building up a modern colossal fortune out of the waste product of the wool washing industry.

It is also about time, though, to destroy these castles in the air by - closing.

BIBLIOGRAPHY.

Archbutt and Dewey - Lubricants and Lubricating Oils.

Allen - Organic Chemical Analysis.

Attfield - General Chemistry.

Analytical Journal - "The Analyst" Vol. 23.

Annal Chim. & Physics. - Vol. 56.

Blount & Bloxam. - Chemistry for Engineers.

Brant - Animal and Vegetable Fats and Oils.

Berichte d. Deutsch Chem. Ges. - All volumes.

Berthelot - Chimie Organique.

Century Dictionary.

Compte Rendu - Vol. 14.

Dispensatory - National Dispensatory.

Gatterman - Organic Chemistry.

Gmelin, Chimie - Vol. 7.

Hammersten - Physiological Chemistry.

Journal Soc. Chem. Industries. Vol. I - XX.

" Amer. " Soc. 1890.

" fur Prakt Chimie. 1868-82.

Ladenburg, Handbook of Chemistry.

Lunge - Industrial Chemistry.

Monatsheft fur Chimie.

Muspratt - Technological Chemistry.

Novy - Physiological Chem.

Newmeister - Physiological Chem.

Payens - Industrial Chemistry.

Pharmacopeia - United States.

" British.

Richter - Organic Chemistry.

Sadtler - Industrial Organic Chemistry.

Thorpe - Dictionary of Indust. Chem.

United States Patent Office Gazette.

" " Twelfth Census Reports.

Watts Dictionary of Chem.

Weidinger - Chemistry.

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